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## MICROSTRUCTURE OF PORCELAIN CONTAINING NEODYMIUM OXIDE

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The effect of neodymium oxide on formation of the microstructure of solid porcelain and the sintering process was investigated. A scheme of the structure- and phase-formation process in solid porcelain with neodymium oxide additive was proposed. It was found that incorporating neodymium oxide in the porcelain paste and increasing the firing temperature cause more active recrystallization of mullite and crystallization of new formations — neodymium orthosilicate — from a glass-phase melt.

The use of different additives that color solid porcelain includes a careful study of their effect on the microstructure of the finished material. Color formation in porcelain containing neodymium oxide, which can change color as a function of the light source, was examined previously. The optimum  $\text{Nd}_2\text{O}_3$  content in porcelain in the amount of 5%<sup>4</sup> was determined and the dependence of the color of articles on the firing medium and light source was also established.

Incorporation of neodymium oxide in sodium-calcium-silicate glasses significantly decreases their viscosity at temperatures above 1000°C and the density increases proportionally to the increase in its concentration in the glass. There are no such studies on incorporation of  $\text{Nd}_2\text{O}_3$  in porcelain, but addition of  $\text{CdO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{ZnO}$ , and  $\text{BaO}$  to a feldspar and porcelain melt is described in [2]; it decreased the initial wetting temperature and viscosity of the glass phase, and thus enhanced the firing process. Addition of small amounts of  $\text{MgO}$  and  $\text{CaO}$  significantly increases the rate of crystallization of mullite.

Equilibrium physicochemical systems have been analyzed and different kinds of interactions of their components proposed: chemical reaction that causes formation of chemical compounds; formation of solid solutions or, in other words, isomorphic mixtures of mixed crystals; absence of any interaction between components in the solid state and their isolation in the form of independent structural constituents of mechanical mixtures. Such an analysis allows determining the conditions of crystallization in a system of both known phases and new phases, which facilitates prediction of the effect of the additives on the system. Incorporation of

additives in porcelain paste significantly affects the structure of the material and consequently also its properties. A classification of additives for porcelain that separates them into four types as a function of the mechanism of action is proposed in [4].

We investigated the effect of neodymium oxide on formation of the microstructure of solid porcelain and its effect on the sintering process.

We used porcelain paste based on the following raw materials (%) as the samples for the study: 35 – 45 kaolin, 5 – 10 clay, 20 – 30 quartz sand, 20 – 30 pegmatite, and also added  $\text{Nd}_2\text{O}_3$  in the amount of 1, 3, 5, 7, 9, and 11%. Porcelain tiles 15 × 15 mm in size and fired at 1350°C (according to the regime: heating for 16 h, cooling for 24 h) and 1410°C (according to the regime: heating for 18 h, cooling for 26 h) were molded for petrography, x-ray diffractometry, and low-vacuum scanning electron microscopy. Porcelain slip powders were prepared from the paste with no  $\text{Nd}_2\text{O}$  (MP) and with a 5% neodymium oxide content were prepared for differential thermal analysis.

The microstructure of the porcelain was investigated with the method in [5] using equipment designed for sample preparation (transparent microsections), VERSAMET-2 optical polarization microscope, and the Buehler-Med automatic image analysis system. As a result of the petrographic study, the phase composition was identified and the semiquantitative composition of the manufactured porcelain (MP) and porcelain containing 5% neodymium (MPN-5) was determined. The number of pores was determined in transient light on transparent microsections (× 284) and the quartz content was determined in transient polarized light also in transparent microsections (× 284).

The change in the structure of the MPN-5 porcelain in comparison to the sample of MP was insignificant (Table 1, Fig. 1) except for the form of the pores, which were basically

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<sup>4</sup> Here and below: mass content.

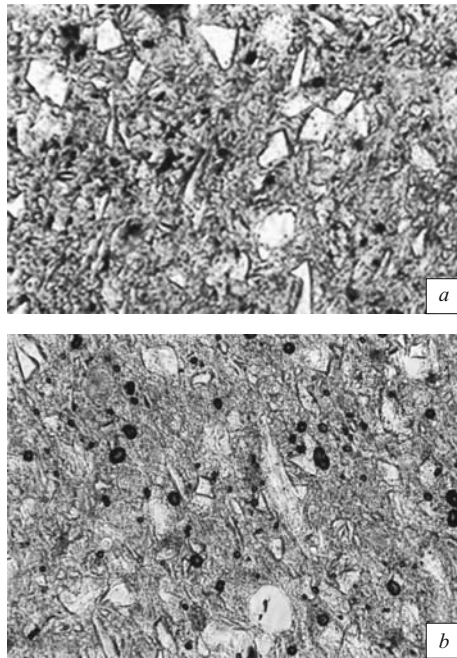


Fig. 1. Structure ( $\times 284$ ) of MP (a) and MPN-5 (b) porcelain.

isolated and well-shaped in MPN-5 (uniform round shape), in contrast to MP porcelain, where the pores were oval and positioned over several pieces. Large round pores were observed in sections of the glassy phase or had a fine border of

TABLE 1

Characteristics of the structure of the porcelain	Porcelain	
	MP	MPN-5*
Amount of residual quartz, %	13.7	12.9
Quartz grain size, $\mu\text{m}$ :		
average	17.5	17.2
maximum	120 – 130	120
Vitrification of quartz grains, $\mu\text{m}$	1 – 2	1 – 2
Porosity, %	7.2	7.2
Pore size, $\mu\text{m}$ :		
average	14.0	15.0
maximum	90 – 100	140
Type of porosity	Isolated and collapsed pores over several pieces	Isolated
Boundaries of pseudomorphoses with respect to feldspar	Preserved	
Network of mullite needles, $\mu\text{m}$	2 – 10 10 – 20	2 – 10 Less commonly 10 – 20
Size of mullite, $\mu\text{m}$	1	< 1
Accumulation of mullite	Local	Reticular, pronounced

\* An increase in the amount of glass phase was observed.

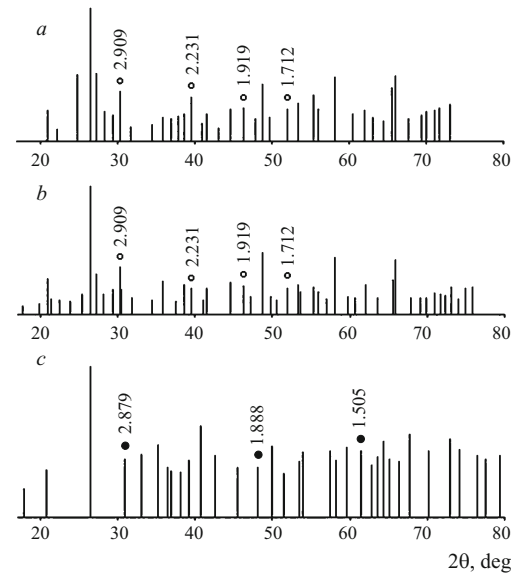


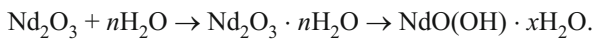
Fig. 2. Line diffraction pattern of samples of porcelain paste dried at  $110^\circ\text{C}$  (a), semifinished product of first firing at  $900^\circ\text{C}$  (b), and porcelain fired at  $1350^\circ\text{C}$  with 5%  $\text{Nd}_2\text{O}_3$  additive (c):  $\circ$   $\text{Nd}_2\text{O}_3$ ;  $\bullet$   $2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2$ .

isotropic small crystals. Note that no crystalline aggregates of  $\text{Nd}_2\text{O}_3$  were found. The oxide probably is either dissolved in the glass phase or forms a finely disperse phase not distinguishable by the given method of analysis.

According to the well-known classification of colored glasses, one of the basic criteria that affect the appearance of color is the ability of the dye to form or to not form its own crystalline phase. These hypotheses were tested with the following methods: x-ray diffractometry (XPA) on a PHILIPS PW-16710 with Crystallographic phase identification software, differential thermal analysis (Bähr DTA-702 system for thermal analysis), and low-vacuum scanning electron microscopy on a JEOL JSM-6480LV instrument with a JED-2300F attachment for energy dispersive spectroscopy. The low-vacuum operating mode allows studying the samples without sputtering a current-conducting layer, while the spectrometer attachment makes it possible to perform a qualitative and quantitative analysis of the composition of solid-state structures both at individual points and in isolated regions.

The crystalline phase of neodymium orthosilicate,  $2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2$ , after firing at  $1350^\circ\text{C}$  was identified by XPA of samples of MPN-5 (Fig. 2). The composition of the orthosilicate was refined, and the composition  $7\text{R}_2\text{O}_3 \cdot 9\text{SiO}_2$  was established instead of  $2\text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$ . The existence of a significant area of homogeneity was characteristic of the former composition. In [6],  $7\text{Nd}_2\text{O}_3 \cdot 9\text{SiO}_2$  or  $7\text{Nd}_{4.67}\text{O}[\text{SiO}_4]_3$  compounds with an apatite-like structure were obtained by sintering  $\text{Nd}_2\text{O}_3$  and  $\text{SiO}_2$  at about  $1200^\circ\text{C}$ . Stability at high temperatures was characteristic of  $7\text{Nd}_2\text{O}_3 \cdot 9\text{SiO}_2$ , i.e.,  $7\text{Nd}_2\text{O}_3 \cdot 9\text{SiO}_2$  melted without decomposing at  $1940^\circ\text{C}$ .

DTA of the samples of MP and MPN-5 showed the presence of several thermal effects. The endothermic effects in the 60–90°C range with maxima at 67°C (MP) and 82°C (MPN-5) were due to loss of physically bound water. The endothermic effect in the 310–350°C region with a peak at 335°C was due to decomposition of neodymium hydroxide, i.e., in prolonged holding in an aqueous suspension,  $\text{Nd}_2\text{O}_3$  can be hydrated. Rare-earth element sesquioxides are typical bases, do not have an amphoteric nature, and their basic character weakens slightly from lanthanum to lutetium. Primarily oxides of the cerium subgroup slowly absorb water vapors in air and are first converted into hydrated oxides, then into hydroxide oxides according to the following reaction:

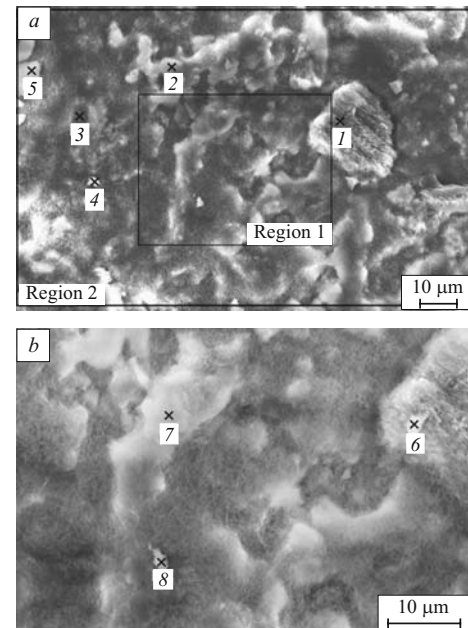


The endothermic effect in the 500–600°C region with a maximum at 550°C is due to dehydration of kaolinite. In this temperature region, slight expansion of the sample was observed, caused by polymorphic transformation of  $\beta$ -quartz into  $\alpha$ -quartz. The endothermic effect caused by the polymorphic transformation of quartz is absorbed by the larger effect of dehydration of kaolinite and formation of meta-kaolinite.

The exothermic effect in the 980–1010°C range with a peak at 997°C corresponds to initial formation of primary mullite and the appearance of a liquid phase [7].

The flattened character of the thermograms of MP porcelain in the 1190–1350°C region indicates intensive glass formation. In phase formation of MPN-5 porcelain, addition of  $\text{Nd}_2\text{O}_3$  shifts the beginning of melting by 40–50°C, probably because of formation of an eutectic in the region of lower temperatures. No other pronounced effects were observed, which could indicate formation of neodymium orthosilicate during cooling of the porcelain, similar to crystallization in cooling in  $\text{Ln}_2\text{O}_3$ – $\text{SiO}_2$  double systems in silicate glasses [8], a typical example of crystallization by growth from a melt [3].

The low-vacuum scanning electron microscopy data suggested the state of the orthosilicate phase in the structure of



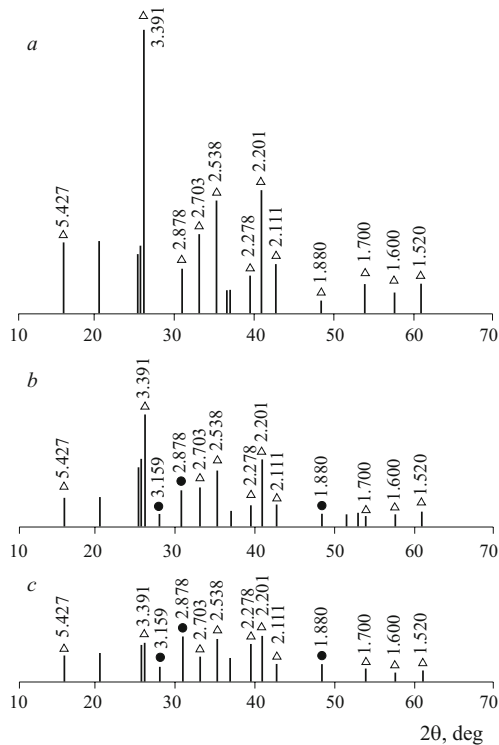
**Fig. 3.** Structure of MPN-5 porcelain (*a*,  $\times 1000$ ), increase in region 1 (*b*,  $\times 2000$ ).

the porcelain. The surface of samples of MPN-5 was analyzed at accelerating voltage of 30 keV in the low-vacuum mode. A pronounced neodymium orthosilicate crystalline phase was not detected in the structure (Fig. 3, Table 2), but spectral elemental analysis revealed undissolved clay particles (points 1, 4, 7), residual quartz (points 5, 6, 8), pseudomorphosis with respect to feldspar (point 2), and sections of glass phase (point 3).

The spectral element analysis of region 2 showed the presence of 3.38% neodymium, or 4.21% in terms of neodymium oxide. These data indicate that the neodymium orthosilicate phase is probably nanosize and for this reason is more uniformly distributed over the glass phase. The small color difference  $\Delta E$  (LAB) [2] of the porcelain samples supports this hypothesis and some investigators think the distribution of the dye concentration in production of color in the glass is described by Fick's differential equations.

**TABLE 2**

Point	Mass content in MPN-5 porcelain, %							
	$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{TiO}_2$	$\text{Nd}_2\text{O}_3$
1	—	—	85.15	14.11	0.74	—	—	—
2	—	4.01	29.49	64.19	2.32	—	—	—
3	2.57	11.59	28.88	51.58	1.18	4.22	—	—
4	—	5.77	50.13	43.01	1.09	—	—	—
5	—	3.86	15.43	76.01	3.68	—	1.01	—
6	—	—	27.91	72.09	—	—	—	—
7	—	—	69.19	30.81	—	—	—	—
8	—	—	27.23	71.09	1.69	—	—	—
Region 2	2.28	5.15	19.40	66.57	1.60	0.78	—	4.21



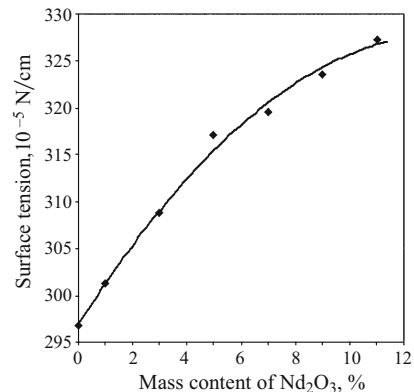
**Fig. 4.** Line x-ray pattern of samples of porcelain fired at 1350°C with no coloring additives — reference (a) and with 5% (b) and 11% (c) neodymium oxide additive: ○)  $3\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ; ●)  $2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2$ .

The most important factors that determine the rate of liquid-phase sintering are characterized in [7]; they are the surface tension and viscosity of the liquid phase and the particle size of the solid phase. The rate of liquid-phase sintering, characterized by shrinkage, is directly proportional to the surface tension on the liquid – solid phase boundary (in the condition of good wetting, i.e., at low surface tension on the liquid – gas boundary) and is inversely proportional to the viscosity of the liquid phase and solid phase particle size.

We can hypothesize that the size of the solid phase particles remained constant. In this case, the viscosity of the liquid phase, which is essentially a function of the temperature, and the surface tension of the melt are of decisive importance for liquid-phase sintering of porcelain containing neodymium oxide. In liquid-phase sintering, the accelerating effect of the temperature on the process is manifested by improvement of the wetting power of the melt, which is due to its surface tension. A. A. Appen proposed the following equation for calculating the surface tension of silicate melts:

$$\sigma_{\text{melt}} = \frac{\sum \bar{\sigma}_i \gamma_{im}}{\sum \gamma_{im}},$$

where  $\sigma_{\text{melt}}$  is the surface tension of the melt,  $10^{-5}$  N/cm;  $\bar{\sigma}_i$  are the specific partial molar coefficients of the surface tension of the corresponding components (oxides) in the



**Fig. 5.** Curve of calculated surface tension (according to A. A. Appen) of porcelain glass-phase melt containing neodymium oxide when the amount is changed.

melt,  $10^{-5}$  N/cm;  $\gamma_{im}$  is the content of each component (oxide) in the melt, mole.

The calculation was performed with data from quantitative-qualitative XPA of porcelain samples with a different  $\text{Nd}_2\text{O}_3$  content, used to determine the crystalline phase content for calculating the glass phase. The x-ray patterns of the samples exhibited clear interplanar distances characteristic of mullite:  $d = 5.427, 3.391, 2.538, 2.201, 2.111$ , and  $1700 \text{ \AA}$  (Fig. 4a), whose intensity decreased with an increase in the concentration of neodymium oxide in the porcelain. The interplanar distances that coincide with the values of neodymium orthosilicate —  $d = 3.159, 2.878$ , and  $1.888 \text{ \AA}$  (Fig. 4b, c), which indicate formation of a given crystalline phase — are an exception. The calculation with the Appen method showed that the surface tension of the melt increased (Fig. 5), the viscosity of the glass phase decreased, and as a consequence, the wetting power of the melt improved and dissolution of small grains of sintered material increased with an increase in the  $\text{Nd}_2\text{O}_3$  content in the porcelain. As a result, the sintering process was enhanced, which increased the apparent density and decreased the porosity of the ceramic material (Fig. 6).

The effect of neodymium oxide on the microstructure of porcelain can be judged by the results of a petrographic analysis of samples of porcelain fired in different conditions. It was found that with an increase in the neodymium oxide content in the porcelain and the firing temperature, the amount of mullite in feldspar pseudomorphoses decreased, while it increased in the glass phase, and in both cases with an increase in the size of the mullite crystals. This is due to a decrease in the viscosity of the glass-phase melt and consequently improvement of transfer of matter for growth of mullite crystals [3]. The increase in the size of the mullite crystals in the pseudomorphoses is due to fusion of the feldspar grain boundaries, which is maximum when the firing temperature is increased and the melt viscosity decreases.

The secondary mullite formed in the glass phase is formed in conditions of significant homogenization of the porcelain paste, and its size also increases with an increase in



the firing temperature and a decrease in the melt viscosity. Based on the morphological traits, secondary mullite is very similar to mullite in feldspar pseudomorphoses, but the grains are usually smaller [9]. The size of the secondary mullite crystals increased from 1–2 to 4–6  $\mu\text{m}$  while the size of mullite crystals in feldspar pseudomorphoses increased from 3–7 to 6–10  $\mu\text{m}$  in samples of porcelain containing 1–11% neodymium oxide and fired at 1350°C in comparison to porcelain without  $\text{Nd}_2\text{O}_3$ .

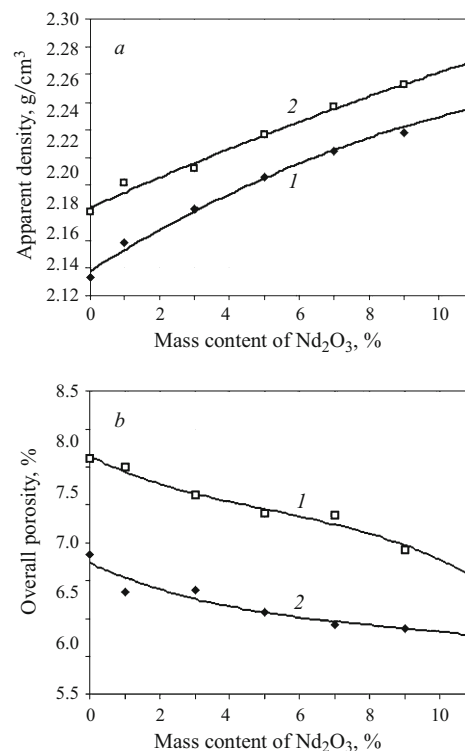
Liquation sections formed at a 9–11%  $\text{Nd}_2\text{O}_3$  content: in samples fired at 1350°C, from 10–20 to 40  $\mu\text{m}$  in size, and in samples fired at 1410°C, up to 60  $\mu\text{m}$  in size. We know that the concentration of segregated material on the surface of mullite crystals indicates the system's attempt to reduce internal energy by decreasing the energy of the glass phase – mullite crystal phase interface, which should remove some of the stresses on the phase interface [7].

The theoretical and experimental studies conducted can be used to represent the following scheme of structure and phase formation in solid porcelain with neodymium oxide additive.

Adding neodymium oxide to the porcelain paste and increasing the firing temperature caused more active recrystallization of mullite and crystallization of a new formation — neodymium orthosilicate — from the glass-phase melt. The change in the microstructure of solid porcelain in addition of neodymium oxide was reflected in an increase in the apparent pore density, size, and shape due to an increase in the surface tension and a decrease in the viscosity of the glass phase.

The effect of addition of neodymium oxide on crystallization of the new formation (neodymium orthosilicate) from the liquid-phase melt on cooling is characterized by a change in the chemical composition and kinetics of the appearance of glass-phase melt (with the participation of the additive). Addition of  $\text{Nd}_2\text{O}_3$  to porcelain in the amount of 5% shifts the initial appearance of the glass-phase melt by 40–50°C in comparison to the glass formation temperature of MP porcelain (1190°C). The acceleration of melting of the glass phase is probably due to the appearance of a eutectic. Earlier formation of the liquid phase intensifies transfer of matter due to diffusion and viscous flow. Neodymium oxide can thus be assigned to additives that enhance sintering, i.e., accelerate the transition from a crystallization to a crystallization-pseudocoagulation structure.

In diffusion of neodymium into aluminosilicate melt, its structure changes, which causes the formation of a phase — neodymium orthosilicate. We should note that when more or less polymerized structures coexist, the less polymerized structures which tend more toward crystallization control the crystallization process. The phase diagram of the system of each elementary section determines the composition of the separated crystalline phases when the melt is cooled to a great degree. In the initial melt forming the porcelain glass phase with the participation of the added neodymium oxide,



**Fig. 6.** Change in the apparent density (a) and overall porosity (b) of porcelain with neodymium oxide as a function of its content and the firing regime: 1) firing in moderately reducing ( $\leq 2\%$  CO) gaseous medium, temperature under 1350°C; 2) firing in strongly reducing ( $\leq 3.5\%$  CO) gaseous medium, temperature under 1410°C.

complete miscibility between the elementary sections should be absent, since two types of crystals at the minimum — secondary mullite and neodymium orthosilicate — are formed from the melt.

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